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A HIGH-TEMPERATURE, FLUIDIZED-BED PROCESS FOR CONVERTING URANIUM DIOXIDE TO URANIUM MONOCARBIDE

by

John T. Holmes, John R. Pavlik,
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Chemical Engineering Division

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SUMMARY

A fluidized-bed process has been studied for the conversion of UO_2 to UC. The process involves making composite particles of UO_2 and graphite and reacting them at 1450-1800°C in a fluidized-bed reactor using an inert gas (helium or argon) for fluidization. High reaction rates can be achieved over a wide range of process conditions. Product purity compares with that obtained in other carbothermic reaction processes. Precise product stoichiometry has not been demonstrated, but is believed to be easily achievable. At the present state of development, bed sintering has not been completely eliminated and thus may prevent rapid removal of all of the reaction product from the fluidized-bed reactor.

I. INTRODUCTION

A high-temperature, fluidized-bed process was investigated for converting UO_2 to UC. Uranium and plutonium monocarbides are potential fuel materials for fast-breeder-reactor power plants. The properties, synthesis, performance and uses of carbide fuels have been reviewed by Holden.[1]

Existing methods for producing uranium (and plutonium) monocarbide involve (1) reaction of the metal with carbon or a hydrocarbon gas, and (2) carbothermic reduction of oxides by using carbon, either in a vacuum furnace or in a furnace provided with an inert-gas flow.

A. Monocarbide from Metallic Sources

Metallic uranium can be reacted with solid carbon by melting in a cold-wall arc furnace to give a monocarbide product of excellent quality.[2] Another process, developed at ANL, involves the reaction of powdered carbon with uranium dissolved in a liquid zinc-magnesium alloy. Carbide made in this way is high in oxygen content (0.4-1.0 wt %) and contains up to 0.5 wt % zinc-magnesium alloy.[3] In both above cases, the chemical reaction is

$$U + C \rightarrow UC.$$
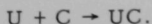
Synthesis of monocarbide by reaction of the metal with a gaseous hydrocarbon gives an excellent powder product for pellet synthesis. Massive metal is first treated with hydrogen at about 250°C to form UH_3 fines. Subsequent reaction with an alkane (methane or propane) at 800°C caused dehydriding and carburization, yielding the monocarbide. The reactions are

$$U_{(massive)} + (3/2)H_2 \xrightarrow{250°C} UH_3;$$

$$UH_3 \xrightarrow{800°C} U_{(powder)} + (3/2)H_2;$$

$$U_{(powder)} + CH_4 \xrightarrow{800°C} UC + 2H_2.$$
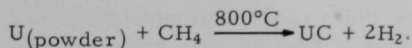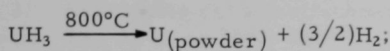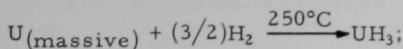
United Nuclear Corp. has used this procedure to prepare about 300 kg of monocarbide, which was used for pellet fabrication.[1]

A fluidized-bed process developed at ANL[4] takes advantage of the more favorable thermodynamics of the carburization reaction at pressures greater than 1 atm. When the reaction of the metal and methane is carried out at pressures above 2 atm, high reaction rates are achieved and a product of controlled stoichiometry and low oxygen and nitrogen content is obtained. This carbide can be pressed directly into pellets without intermediate milling or binder addition. The ANL fluidized-bed process has been demonstrated for UC and mixed (U,Pu)C.

B. <u>Monocarbide from Oxide Sources</u>

The production of UC from UO_2 involves heating pelletized UO_2-carbon mixtures in a furnace at 1400-2000°C. The carbothermic reaction is

$$UO_2 + 3C \rightleftharpoons UC + 2CO.$$
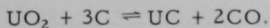
Either a vacuum or a flowing inert gas is used to remove the CO reaction product and prevent back reaction.

Westinghouse[5] has considered using a continuous-belt, tunnel furnace with an argon carrier gas for production of fuel for a 200-MW(e) demonstration fast breeder power reactor. United Nuclear Corp.[6] is making UC and PuC in a vacuum furnace in kilogram quantities for irradiation testing. Himmelstein et al.[7] operated a semicontinuous vacuum reaction furnace, which has a production capacity of 3 kg of UC per hour. The product from the carbothermic reduction of oxides is inferior in purity (high oxygen content) to material produced by the metal-alkane route.

The British have studied the use of fluidized beds for conducting carbothermic reductions to produce uranium carbide, nitride, and carbonitride. Hyde et al.[8] used a 1-in.-ID graphite fluidized bed, which had a capacity of about 40 g per run; Fletcher et al.[9] used a 3/4-in.-ID fluidized bed which

had a capacity of about 10 g per run. Observations from both studies include the following:

1. Bed sintering occurred in most runs, although there appeared to be solutions to this problem.

2. The reactor walls contributed significant amounts of carbon to the reaction.

3. Acceptable carbon stoichiometry and low oxygen contents were achieved in 3 to $3\frac{1}{2}$ hr at 1500-1800°C.

The main objective of our study was to develop improved methods for converting mixed uranium and plutonium oxides to carbide fuel for fast reactors. Although the experimental work with the fluidized-bed reactor was concerned only with conversion of UO_2 to UC, the results are thought to be indicative of those expected for conversion of UO_2-PuO_2 mixtures to (U,Pu)C. The reaction was conducted in a fluidized bed, which allowed intermittent discharge of the product and recharging of the bed without cooling. Thus, the process was expected to be capable of high production rates in compact equipment suitable for semiremote synthesis of fuel. An inert carrier gas was used to fluidize the bed and remove CO. This means of CO removal should result in lower plutonium volatilization losses, if the process is used for PuC or (U,Pu)C production, than those that occur in the classical vacuum reduction process. The fluidized-bed process described in this report closely parallels some of the British fluidized-bed work,[8,9] but was carried out on a larger scale.

II. EQUIPMENT AND PROCEDURE

A. Fluidized-bed Reactor

A fluidized-bed reactor was available from another project. This reactor had been constructed to study the production of UC from UO_2 formed by the fluidized-bed reduction of UF_6 with steam and hydrogen. The UO_2 formed by that method is directly suitable for carbiding in a fluidized bed if carbon can be added from the fluidizing gas rather than by mixing graphite with the fuel material. For such UO_2 feed material, carbon might be added in the form of methane in a CH_4-H_2 fluidizing gas. Thermodynamic calculations indicated that at high pressures (10 atm) and high hydrogen concentrations ($\sim$98-99%), carbon deposition could be avoided under conditions that would result in rapid carbide formation. Since experimental work was not undertaken for that process, the reactor was available for this study.

The reactor had a 2-in.-ID fluidized-bed section and was capable of being operated at up to 2000°C and 10 atm. The reactor is shown schematically in Fig. 1. The fluidized-bed section and the heating element that

CHARGE HOLDER

SIGHT PORT

GAS EXIT

DISENGAGING SECTION

INSULATION

2- IN ID GRAPHITE FLUID BED REACTOR

GRAPHITE HEATER

VACUUM PORT

PRESSURE VESSEL

POWER LEADS

INLET STEM ADJUSTMENT

GAS INLET

308-1524

PRODUCT RECEIVER
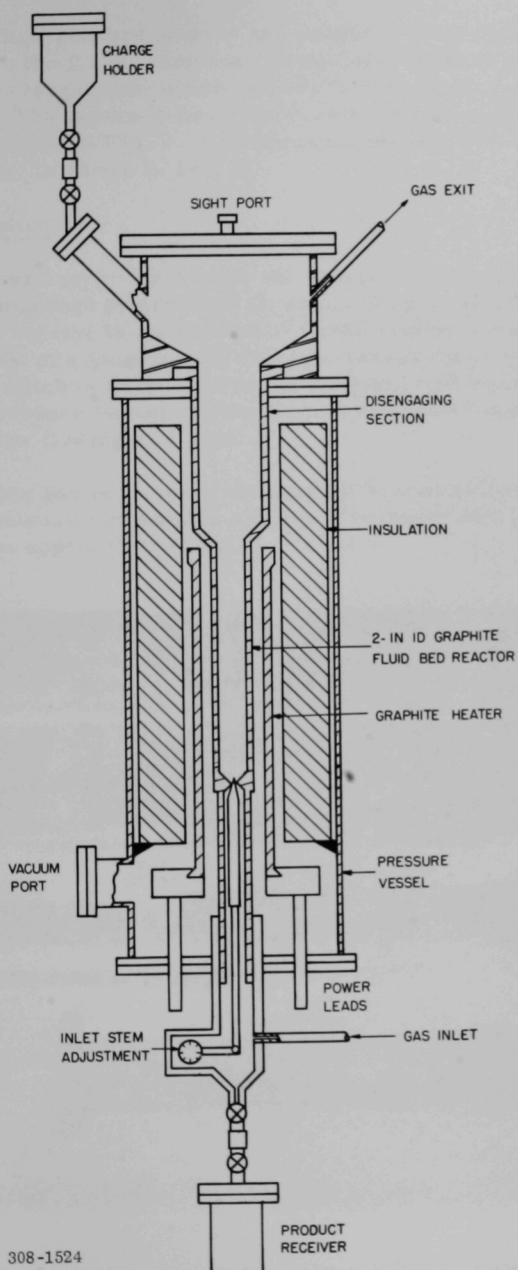
Fig. 1. Fluidized-bed Reactor Used for UO_2-Carbon Reactor Study

surrounds the fluidized-bed section are constructed of high-density graphite. The inlet to the fluidization zone is equipped with an adjustable valve stem and plug arrangement, which is used to contain or remove the fluidized particles. The fluidized-bed components, heater, and graphite-wool insulation are shown in Fig. 2. The pressure vessel, which contains the 2-in.-ID reactor, is shown in Fig. 3.

B. Instrumentation

The power supply for heating the reactor is a three-phase, low-voltage, high-amperage system with an output of up to 36 kVA. The temperature of the reactor is automatically controlled by a controller, which senses the output of a tungsten-5% rhenium versus tungsten-26% rhenium thermocouple, which is positioned in the fluidized bed inside a molybdenum sheath. The pressure vessel, power supply, and power feed-throughs are cooled with water flowing at 4 gpm.

Fluidizing gas is metered through calibrated rotameters and is controlled by manually adjustable valves. Pressures and pressure drops are indicated on appropriate gauges.
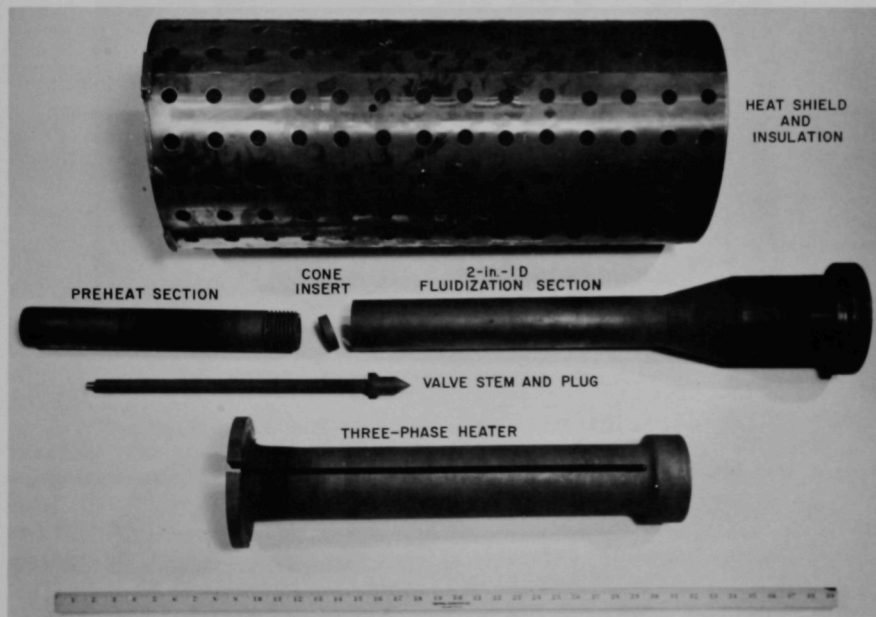
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Fig. 2. Graphite Components and Insulation Used in High-temperature, Fluidized-bed Apparatus

308-997A

Fig. 3. High-temperature, Fluidized-bed Reactor Installation

The reaction is monitored by analysis of the effluent gas from the reactor. The reaction of UO_2 and carbon produces CO, which is continuously measured by a water-cooled, Gow-Mac GBT thermal-conductivity cell. The fluidizing gas (helium or argon) is used as the reference gas, and the CO-fluidizing gas mixture is the sample gas. A process gas chromatograph (Process Analysers Inc.) is also used to measure the CO concentration on an intermittent basis. The chromatograph automatically samples and analyzes the reactor effluent gas at 6-min intervals. The unit is capable of simulatneous CH_4, argon, hydrogen, CO, and CO_2 analyses. Figure 4 is a schematic flow diagram of the effluent-gas analysis system.
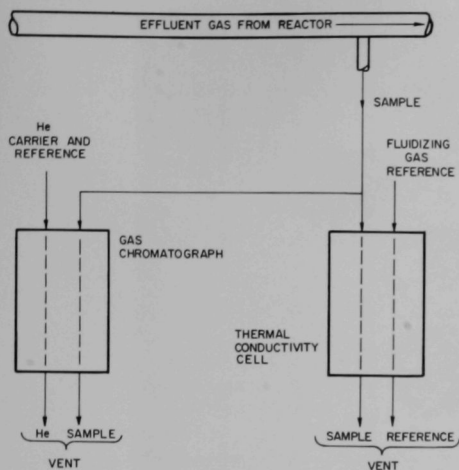
308-1523

Fig. 4. Gas Analysis System for UO_2-Carbon Reaction

C. Procedures

1. Production of Reactant Particles for Fluidization

Fluidizable particles of UO_2 and graphite are made by dry-blending the oxide, carbon, and a small amount of polyvinyl alcohol (PVA) binder, followed by adding water to dissolve the binder and thus promote agglomeration of particles suitable for fluidization. The blending and agglomeration operations are performed in a Patterson-Kelly twin-shell blender. The UO_2, carbon, and PVA are first dry-blended for at least 16 hr. Distilled water is added in incremental amounts to the tumbling material in the blender until small spheres are formed. Continued tumbling produces larger particles, and the process is stopped when particles of the appropriate size are formed. The particles are dried at 50°C for at least 16 hr and separated by sieving. The resulting particles have a bulk density of about 1.8 g/cc and a particle density of about 3.1 g/cc.

Table I presents the compositions of the two batches of particles used in this study. Typical particles are shown in Fig. 5. Strausberg[10] reported that PVA contributes 10% of its initial weight as carbon, which is available as a reactant; the remainder is volatilized during the reaction. The expected stoichiometry was calculated by assuming all oxygen in excess of stoichiometric $UO_{2.00}$ and all oxygen in the graphite react to give CO_2.[10]

TABLE I. Composition of UO_2-Carbon Particles Used for Fluidized-bed Production of UC

| Batch | UO_2 | | | Graphite | | Polyvinyl Alcohol (wt % in Batch) | Expected Product Stoichiometry[a] | |
	Source	O/U	wt % in Batch	Source	wt % in Batch		C/U	wt % C
A	NUMEC	2.12	82.0	National Carbon Grade 38 (0.008% O)	11.6	6.4	1.32	6.23
B	NUMEC	2.01	85.1	National Carbon Grade 38 (0.008% O)	10.6	4.2	0.907	4.37

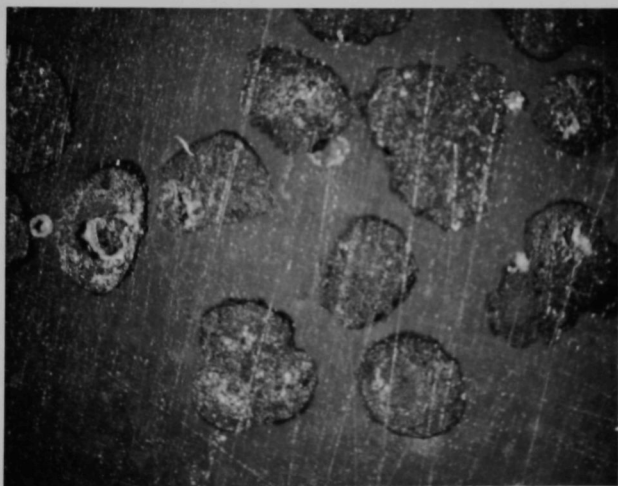[a]Assuming reaction goes to completion, and PVA contributes 10% of its weight as available carbon.[10]

13X

Typical 0.71-1.00-mm Particles on a 1-mm Grid

20X

Cross Sections of 0.71-1.00-mm Particles

Fig. 5. Uranium Oxide-Graphite Agglomerates
Used for Fluidized-bed Reaction Studies

The available carbon comes from the graphite and 10% of the PVA. Batch A was formulated with 32% excess carbon, and batch B was made about 9% deficient in carbon.

2. Run Procedure

The procedure for initiating a run consists of evacuating the reactor and pressure vessel, checking for leaks, and refilling the reactor and pressure vessel with the inert fluidizing gas. The heat is then turned on, and the reactor is heated to operating temperature (1450-1800°C), which takes about 1 hr. The flowrate of fluidizing gas is adjusted to the desired value, and the charge of UO_2-carbon particles is admitted to the reactor. The reaction is monitored by the thermal-conductivity cell and the gas chromatograph. The quality of fluidization is observed through a sight port, which allows viewing of the top surface of the bed. As the reaction proceeds, the fluidizing-gas flowrate must be increased to maintain good fluidization. The increase is required because of the higher density of the product particles and probably also because of the presence of multi-particle clumps, which are formed by particle-to-particle sintering. The run is terminated when the rate of CO evolution becomes insignificant. The free-flowing product is removed from the reactor, without cooling down the reactor, by lowering the plug at the inlet to the bed.

3. Run Conditions

Twelve runs were made in this program. The operating conditions and some of the results are given in Table II. In most runs, the temperature was held constant (within ±10°C) throughout the reaction period. In Runs 2, 3, 4, and 7, the temperature was increased near the end of the run in an attempt to speed up the reaction. The superficial gas velocity, under reaction conditions, was as low as 2.4 ft/sec of argon for Run 1 and as high as 21 ft/sec of helium for Runs 10 and 11. The particle size varied from 0.71-1.00 mm in Run 1 to 1.41-2.00 mm in Runs 10, 11, and 12. In Run 6, hydrogen was used as the fluidizing gas for the final 30 min in an attempt to free a sintered bed. An intermittent methane treatment was used in Runs 7 and 8 in attempts to prevent sintering by depositing excess carbon on the outside of the particles. Powdered nickel, a sintering aid, was added to the feed particles in Run 8. The pressure in the fluidized bed was 1-3 psi above atmospheric pressure in all runs.

III. RESULTS AND DISCUSSION

The rate of reaction in all runs was relatively fast. Projections to plant scale indicate that at least 30 kg/day of UC could be produced in a 12-in.-diam fluidized-bed reactor. Table II gives analytical results of the product particles and operational results for the 12 runs.

TABLE II. Operating Conditions and Results for Fluidized-bed Conversion of UO_2 to UC

Run	Time (min)	Fluidized-bed Temperature (°C) Av	Max	Superficial Gas Velocity (ft/sec)	Particle Size (mm)	Carbon Content (% excess)	Initial Charge to Bed (g)	Additives	Analysis of Product[a] Oxygen (wt %)	Carbon (wt %)	Operational Results
1	50	1200-1860	1860	~2.4 (Ar)	0.71-1.00	32	200	None	N.S.	N.S.	30% of product sintered to walls; remainder probably elutriated to filter.
2	240	1500	1560	~2.3 (Ar)	1.00-1.41	32	200	None	1.4	6.65	After cool-down, 70% of product sintered to walls, 30% free-flowing.
3	180	1550	1610	~3.1 (Ar)	1.00-1.41	32	188.3	None	0.48	6.26	After cool-down, 10% of product sintered to walls, 90% free-flowing.
4	300	1550	1610	~2.8 (He)	1.00-1.41	32	~190	None	0.44	6.31	After cool-down, 45% of product sintered to walls, 55% free-flowing.
5	480	1550	1550	~6.4 (He)	1.00-1.41	32	190.3	None	0.75	6.56	Bed charged to hot reactor; after cool-down, 85% of product sintered to walls, 15% free-flowing (11% free-flowing hot).
6	86	1560	1560	~7.5 (He)	1.00-1.41	9	716.9	H_2 gas, final 30 min	N.S.	N.S.	Bed completely sintered after 36 min; H_2 flow did not free sinter.
7	330	1550	1650	~12.4 (He)	1.00-1.41	9	200	CH_4 1 min on 9 min off	0.38 Free, 0.27 Sintered	9.0 Free, 6.8 Sintered	Bed completely sintered at end; CH_4 may have delayed sintering. Some loose particles after cool-down.
8	215	1550	1550	~8 (Ar)	1.00-1.41	9	200	Ni in particles; CH_4 in gas; new reactor tube	0.22	6.7	Bed completely sintered about 200 min after startup.
9	28	1820	1820	~8 (Ar)	1.00-1.41	From Run 6	310 from Run 6	None	N.S.	N.S.	Bed started sintering 2 min after startup.
10	9	1800	1800	~21 (He)	1.41-2.00	9	289	None	N.S.	N.S.	Bed completely sintered 8 min after startup.
11	240	1560	1570	~21 (He)	1.41-2.00	9	289	None	0.40	4.94	Bed appeared fluidized but partially sintered under top of bed; most of bed free-flowing while hot.
12	450	1450	1460	~12 (He)	1.41-2.00	9	621	None	0.78	5.27	Only few dozen particles stuck to wall at end of run.

[a]N.S. = Not submitted.

Sintering of the particles occurred in each run. Usually, near the end of the run, particles would stick to the graphite reactor walls or to the molybdenum thermocouple well. Other particles would sinter to previously immobilized particles until the bed was completely or at least partially immobilized. Bed sintering prevents rapid removal of the product and therefore makes this fluidized-bed process at its present state of development no more attractive than existing batch or semicontinuous processes. Similar sintering effects in fluidized beds were noted by the British,[8,9] and by Himmelstein et al.[7] in their semicontinuous vacuum reactor.

Most of the runs in this study were made in an attempt to prevent bed sintering. The use of (1) helium rather than argon; (2) large, rather than small, particles (Runs 10-12 versus 1-9); (3) less than a

stoichiometric amount of carbon in the reactant particles (Runs 6-12 versus 1-5); (4) a hydrogen or methane gas treatment (Runs 6-8); (5) a deep (Runs 6-12), rather than shallow, bed; (6) nickel sintering aid in the particles (Run 8); (7) high temperatures, 1800°C, for fast reaction (Runs 1, 9, and 10); and (8) low temperatures, 1450°C (Run 12), were all ineffective in completely preventing sintering.

The best run with regard to absence of sintering was Run 12, which was carried out at 1450°C, the lowest temperature in the series, and with the largest particles, 1.41-2.00 mm. Only a few dozen particles were stuck to the reactor wall at the end of the run. Possibly many similar runs could be carried out before lowering the reaction temperature for removal of the sintered materials. Although the amount of sintering was small, the residual oxygen content after a long reaction period of 450 min was unacceptably high at 0.78 wt % (7800 ppm). Based on observed difficulties in sintering $(U,Pu)C$, possibly bed sintering would not be a problem if mixed UO_2-PuO_2 were used for the starting material rather than UO_2 alone. Investigation of this possibility was beyond the scope of this study.

Oxygen analysis showed that the lowest residual oxygen content, 0.22 wt % (2200 ppm), was achieved in Run 8, in which nickel was added to the particles. Hanson[11] noted improved oxygen removal when sintering aids were added to the other reactants. The lowest oxygen content for the runs not containing nickel was 0.38 wt % (3800 ppm) in Run 7, in which a large excess of carbon was available as a result of an intermittent methane-gas treatment. The residual oxygen in the carbide product from this process is about a factor of ten higher than that achieved in the metal-alkane reaction process,[4] but the lower oxygen contents achieved in this study compare quite well to the purity of carbide produced by other carbothermic reduction processes.[1]

The stoichiometry of the reaction product is close to that expected on the basis of complete reaction of the starting materials and allowing for the unreacted oxygen. In Runs 11 and 12, the product would be about 0.3 wt % higher in carbon than expected from the quantity of carbon in the original particles. The carbon content would be 0.23-0.63 wt % lower than expected in Runs 2 through 5. In smaller-scale equipment, Hyde[8] found that about 15% of the carbon in his product came from attrition of the graphite reactor walls. This effect may be insignificant in our larger-scale equipment. More exact stoichiometry control might be achieved by variation of the composition of the fluidized particles. Excess carbon, if present, probably could be removed by a hydrogen treatment at 800°C to give stoichiometric UC.[4]

IV. CONCLUSIONS

The fluidized-bed process is capable of high production rates and gives a product of purity comparable to that obtained from other carbo-thermic reduction processes. Precise control of the stoichiometry may be achieved by adjusting the amount of carbon supplied in the reactant particles. Bed sintering has not been eliminated and thus prevents rapid removal of all of the reaction product from the reactor at temperature levels at which low oxygen content can be attained (1550°C).

ACKNOWLEDGMENT

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